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Photon echoes and optical detrapping in solids

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1982

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Morsink, J. B. W. (1982). Photon echoes and optical detrapping in solids. s.n.

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CHAPTER 1

INTRODUCTION AND SUMMARY

1.1. Introduction.

The study of the interaction of electromagnetic radiation and matter provides a means to extract information about structure and dynamics of molecules. The optical spectroscopy of mixed molecular crystals at low temperature, in which we are especially interested, forms part of such a kind of research.

Initially, spectroscopists only had the availability of incoherent light sources with relatively low intensity for excitation of the samples. Molecular information had to be derived predominantly from data gathered in the frequency domain. McClure [2] was the first who showed that from mixed molecular crystals at low temperature (≤ 4.5 K) sharp line spectra (~ 0.5 - few cm^{-1}) of the electronic transitions of guest molecules can be obtained. However, the information derived from such spectral lines is to a large extent restricted to static properties of the molecules. Extracting data about dynamic properties, related to the widths of the lines, was, until recently, much more of a problem.

Time dependent processes, by the uncertainty principle [3], give rise to a finite linewidth of an optical transition. At low temperature, however, very often these so-called homogeneous lineshapes of electronic transitions cannot be observed by conventional spectroscopic methods. Crystal strain gives

effectively a static distribution of transition frequencies of the ensemble of molecules under study. The homogeneous lineshape may then be hidden by an inhomogeneous broadening. Upon raising the temperature, the homogeneous linewidth broadens such that, in principle, a study by conventional spectroscopic methods becomes possible. However, as the complexity of the relaxation processes operant also increases with temperature, it is preferable first to gain insight in the low temperature relaxation mechanisms.

Relaxation processes in an optical transition of a mixed molecular crystal may be divided, in analogy with magnetic resonance [4] into two categories [5]. When there is a net transfer of energy from the system under study (e.g. a molecule) to its surrounding (the bath) then such a process may be classified as T_1 -relaxation. In molecules this can happen via radiative (fluorescence or phosphorescence) and radiationless (internal conversion and intersystem crossing) relaxation.

On the other hand, due to the interacting of the bath and the molecule considered, fluctuations in the frequency of the optical transition may appear. Among these interactions there are phonon scattering, intermolecular coupling within the ensemble of excited molecules and spin-dependent interactions. These processes are often referred to as pure dephasing or T_2^* -relaxation. There may be exchange of energy between the molecule and bath, but there is no net transfer of energy.

With the advent of the laser, optical spectroscopy rapidly developed. By the special characteristics of laser radiation, it became possible to improve conventional spectroscopic methods and to initiate new ones. In particular, a detailed research of the dynamics properties of molecules could be done. Now, by fluorescence line narrowing [6] and hole burning [7] techniques, in the frequency domain the homogeneous lineshape from an inhomogeneous broadened transition can be extracted. Furthermore, in analogy with the magnetic resonance, coherent spectroscopy at optical frequencies is feasible. Photon echo [8] and optical free induction decay [7b, 9] are examples of such coherent techniques which prove to be very fruitful in studying dynamic interaction processes. A general review of recent application of them can be found in an article by Shoemaker [10]. The photon echo, in particular, is used for the research described in this thesis.

Briefly, the photon echo effect may be described as follows. A photon

echo can be generated in a system with an inhomogeneously broadened optical transition. The signal consists of a pulse of radiation emitted after the sample has been excited by two or more time-separated coherent (laser) pulses. In a two pulse photon echo (2PE) [8] experiment, the first excitation pulse creates a macroscopic polarization; the transition moments of all absorbing molecules oscillate in phase. After this pulse the phase relaxation among these molecules is rapidly lost due to the spread in transition frequencies (inhomogeneous dephasing). After a brief waiting period, a second pulse is applied and this inhomogeneous dephasing process will be reversed. After the same period a macroscopic polarization is again generated in the sample, which leads to the echo signal emitted. Note that the echo appears at twice the waiting period, because the inhomogeneous dephasing and rephasing rates are the same. From this description, it will be clear that the echo signal is extremely sensitive to the phase relaxation of the excited molecules. The T_2^* -processes which we described before are totally uncorrelated and lead to irreversible dephasing. Molecules that undergo such processes will be lost from the generation of the echo signal. From measurements of the echo signal as a function of pulse separation or temperature, information about T_2^* -processes can be obtained. Of course, the echo signal will also be sensitive to T_1 -relaxation, which places an upper limit on the echo lifetime.

In a three pulse stimulated echo (3PSE) experiment the echo signal is generated from three excitation pulses [11]. Whereas the second pulse in a 2PE reverses the inhomogeneous dephasing, in a 3PSE it renders the coherence insensitive to phase fluctuations until the third pulse initiates the rephasing. After a while, an echo will again appear at the maximum of rephasing. Between the second and third pulse, the coherence information is stored in the form of a population distribution within in the inhomogeneous broadened absorption line: a grating. That is why, homogeneous dephasing is not effective during this period and the echo signal will only be sensitive for changes in population distribution. The 3PSE can therefore be used for measuring T_1 and spectral diffusion processes within the inhomogeneously broadened absorber [11, 12].

Since the first successful detection of a photon echo by Kurnit, Abella and Hartmann [8a], this phenomenon has been extensively used for gaining information about dephasing in optical transitions. After tunable dye lasers

became available, the photon echo was applied on mixed molecular crystals by Aartsma and Wiersma [13]. At low temperature (< 5 K) nanosecond dephasing on origins of electronic transitions in some systems was studied. Hesselink and Wiersma [14] extended this research to the picosecond domain so that dephasing on pure electronic transitions could be followed up to higher temperatures (~ 20 K). Even dephasing of vibrational transitions could be studied. Meanwhile in our laboratory theoretical models for optical dephasing and relaxation in mixed molecular crystals were also developed [15]. These photon echo investigations in molecular solids were recently reviewed in Ref. 16.

The photon echo studies summarized so far have been performed on more or less two-level-like transitions. The echo time evolution becomes different if more than only one ground- and one upper state becomes excited. In such a case, modulations in the echo decay can appear. This is a result of quantum mechanical interference that occurs when two or more closely spaced transitions with a common level are excited coherently. Theoretically and experimentally, these effects have been examined before [17].

Next to these modulation effects, in one of those systems a very long lived 3PSE signal was observed [18], but as yet no explanation for this phenomenon had been found. This led us to perform a 3PSE study in systems with a multilevel structure.

Besides these investigations on more or less isolated molecules, we also studied molecules where intermolecular interactions play a very dominant role in the structure of the energy levels.

A laser induced energy transfer technique was applied for revealing information about the level structure in a molecular exciton band. Due to the optical $\vec{k} = 0$ selection rule, most states in an exciton band are not easily accessible with conventional spectroscopic techniques. However, via an optical detrapping process we were able to probe separately all \vec{k} states of a singlet exciton band. This detrapping process could be induced by an intense laser field. The feasibility of intermolecular electronic energy transfer under influence of an optical radiation field had been predicted before [19] and shortly thereafter it was observed in the gas phase [20], but the observation and application of laser induced energy transfer (LIET) in a solid is new [21].

Furthermore, in more diluted system we studied the dynamics of inter-

molecular interaction. Again the photon echo was used for an investigation of optical dephasing in a highly concentrated crystal and in a molecular dimer pair.

1.2. Summary.

This thesis is organized as follows. In Chapter 2 the laser set-up, experimental procedure and sample details are discussed. Because echo generation on a nanosecond time scale had been done before at our laboratory, it is only briefly described. The equipment for the generation of a LIET signal is a simple variation on the echo set-up. More attention has been paid to describing modifications in the system, which have been applied during the course of this research project. Finally, we had at our disposal a computer to automate the experiments and for digital data acquisition. The mixed crystals that we have examined are discussed in Fig. 1.1.

The description of the 2PE and 3PSE decay in a transition with a nearly degenerate level structure in ground- and excited state is one of the major subjects of Chapter 3. Relaxation effects are ignored, but it will be shown that a photon echo by its coherent property can unravel important hyperfine splitting data from an inhomogeneous broadened transition. Although we are principally interested in organic molecules the photon echo data obtained on the hyperfine splitted $^3P_0 + ^3H_4$ transition of Pr^{3+} in LaF_3 are relevant to this discussion, that is why we included them in this chapter.

In Chapter 4, the problem of the long lived 3PSE phenomenon is tackled. With a density matrix method, the photon echo time evolution in a three level model system, including decay has been calculated. From this analysis it became clear that optical coherence can be stored in a spin population distribution. The lifetime of this so-called anomalous photon echo is restricted by spin relaxation processes only. In this chapter the observations of this echo phenomenon in triphenylmethyl in triphenylamine (TPM in TPA) and Pr^{3+} in LaF_3 will also be discussed. In fact, the same 3PSE feature appears in molecules with a triplet bottle-neck. It will be shown for pentacene in naphthalene and naphthalene in durene that the long lived echo can be helpful in determining rate parameters for intersystem crossing.

In Chapter 5, it is demonstrated that it is possible to transfer energy from S_1 excited pentacene guest molecules to states in the S_1 exciton band of

from phonon assisted scattering of the excitation into the spectroscopically non-observable other dimer state.

1.3. Conclusions.

The experimental results of the 2PE and 3PSE studies on transitions with a multilevel structure have shown that the photon echo is not only a useful probe for optical dephasing, but also that important information about the multilevel structure itself can be obtained. In cases where such level splittings are of magnetic origin, not only the echo decay, but also experiments with the echo intensity as a function of magnetic field can be very informative.

The results of the calculations on a multilevel model system contributed in understanding the anomalous 3PSE effect. The storage of optical coherence in transitions with optical branching now seems to be well understood. For a complete picture of the optical dephasing in system, whose transitions show such a branched structure more experimental research is required.

The feasibility of optical detrapping in solids not only has been shown, but it also became evident that it can be applied to extract information about exciton bands. The model developed here for laser induced intermolecular coupling is somewhat preliminary and needs more attention in future investigations.

In spite of our efforts the observed lifetime shortening of the 2PE in highly doped crystals has not given a clear picture of the optical dephasing mechanism. If indeed intermolecular interaction is effective, the delocalization of the excitation may be responsible, at least that is what we observed for a dimer. In general, the most important problem, theoretically and experimentally, will be to take into account doubly and multiply excited states.

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